The Mechanism of Green Light Emissions from Alx Ga1-x P-GaP Liquid Phase Epitaxial Layers(AlxGa1-x P-GaP 液相エピタキシャル層の緑色発光機構)

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GaP and $Al_xGa_{1-x}P$ are important materials in green light emission field. For the great advantages of low cost and mass production being realized easily, efficient GaP pure green LEDs fabricated by liquid phase epitaxy on GaP substrates with temperature difference method under controlled vapor pressure (TDM-CVP) are most widely applied. More and more requirements of higher brightness green light emission diodes and shorter wavelength green LEDs have promoted the researches on optical property of GaP and AlGaP alloy since 1960s. However, the fact that GaP is an indirect band structure semiconductor, brings about more difficulties in improving the green light luminescence efficiency of GaP LEDs. And, the fact that lack of an liquid phase epitaxy technology in fabricating well-distributed Al composed layer, so that almost no detailed research on luminescence mechanism of $Al_xGa_{1-x}P$ alloy has been reported.

In this thesis research, for revealing the possibilities of realizing shorter wavelength green light emitting diode with $Al_xGa_{1-x}P$ and high efficiency of green light emitting from GaP in $Al_xGa_{1-x}P$-GaP heterostructures, we fabricated homogeneously Al composed $Al_xGa_{1-x}P$ layers and good quality $Al_xGa_{1-x}P$-GaP heterostructures with TDM-CVP liquid phase epitaxy technology, and investigated their luminescence properties with photoluminescence measurements and absorption measurements.

Chapter 1, the introduction to the thesis, states the background and purpose of this research.

Chapter 2, the methods of crystal growth and crystal characterization, includs an explanation of principals and processes of TDM-CVP liquid phase epitaxy application to $Al_xGa_{1-x}P$ layers and $Al_xGa_{1-x}P$-GaP heterostructures, the methods of photoluminescence measurements and absorption spectrum analysis. Homogeneously Al composed $Al_xGa_{1-x}P$ liquid phase epitaxial layers are essential for investigating Al_xGa_{1-}

$_x$P luminescence properties, and have been difficult to be realized by conventional LPE technologies. We predict that homogeneously Al composed layers can be fabricated succesfully during the fixed temperature growth process in TDM-CVP LPE, which is confirmed by the results of EPMA given in Chapter 3.

Chapter 3, luminescence mechanism of $Al_xGa_{1-x}P$ liquid phase epitaxial layers, gives main research results of photoluminescence from $Al_xGa_{1-x}P$ liquid phase epitaxial layers. Our study on $Al_xGa_{1-x}P$ photoluminescence, along with absorption spectrum analysis, has firstly clarified that free exciton recombination without phonon assistance is an important mechanism in $Al_xGa_{1-x}P$ luminescence at 77K, and becomes dominant at room temperature. Al composition dependence, temperature dependence and ion density dependence of this luminescence have been discussed, and the main results are summarized below,

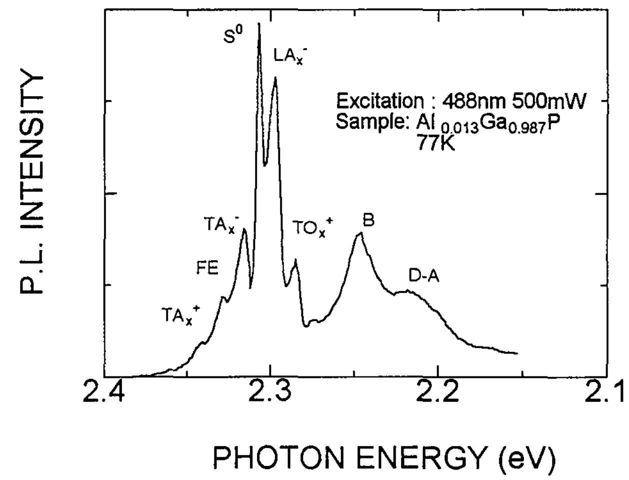

Fig.1 P.L. Spectrum of $Al_xGa_{1-x}P$ at 77K

1. The free exciton recombination luminescence without phonon assistance shows following characterizations of its free exciton nature at 77K:

(1) Luminescence peak energy position is at the center of the ones of TA_x phonon emission and absorption.

(2) Luminescence peak shape shows its energy distribution following a Boltzman function of free exciton kinetic energy

(3) Luminescence intensity is directly proportional to excitation power.

2. This zero-phonon free exciton recombination luminescence shows very clear Al composition dependence as

(1) Peak intensity increase with Al composition

(2) Peak broadens with Al composition

(3) Peak energy position shifts to higher energy linearly when Al composition becomes larger

suggesting that the mechanism of this non-phonon free exciton recombination transition probability increase for the reason of introduction of Al atoms in crystal. The perturbation to electron potential is considered to be the mechanism that Al atoms act on free carriers.

3. Ion density dependence of photoluminescence, that the ratio of FE peak intensity and bound exciton peak intensity decreases with the minus 0.5th power of net ion density in epitaxial layer.

4. Photoluminescence temperature dependence confirms the dominant roles of free exciton recombinations with phonon assistance, as well as the phononless free exciton recombinations. Room temperature luminescence intensities have a peak at an Al composition of about 0.1, which is thought as a result of stronger effect of deep levels as non-radiative centers at room temperature.

5. The result of PHCAP measurement shows that a deep level of 1.6eV below conduction band is related to the Al in $Al_xGa_{1-x}P$ epitaxial layers.

6. Detection of zero-phonon free exciton transition in $Al_xGa_{1-x}P$ absorption spectrum at 77K confirms again phononless free exciton recombination as an important luminescence mechanism of $Al_xGa_{1-x}P$ LPE layers.

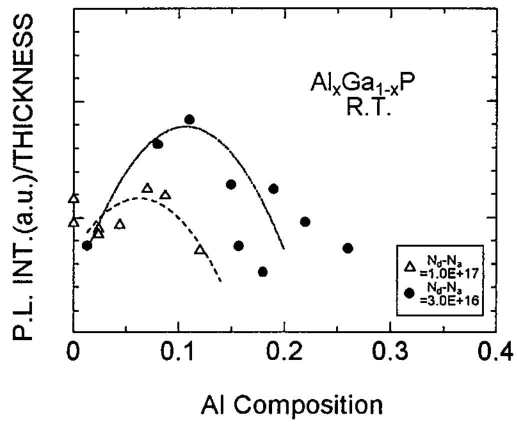

Fig.2 P.L. Intensity Dependence on Al Composition

Chapter 4, Luminescence from $Al_xGa_{1-x}P$-GaP heterostructures, is the summary of results on photoluminescence study on $Al_xGa_{1-x}P$-GaP heterostructures. It is well known that GaP luminescence from free exciton recombination with phonon assistance. The potential barriers at the interfaces of GaP and $Al_xGa_{1-x}P$ are expected to block free carriers as well as the free excitons diffusing from luminescent layer in heterostructures. Our comparative study on photoluminescence from homostructure, single heterostructure and double heterostructure of $Al_xGa_{1-x}P$-GaP confirmed that such a carrier confinement effect enhances photoluminescence intensity, and the temperature dependence and impurity effect on photoluminescence in heterostructures are obtained also for understanding luminescence mechanism. Main results are summarized as:

1. Efficient green light emission from GaP-$Al_xGa_{1-x}P$ double heterostructures is observed when the luminescent GaP layer is as thin as 4μm, while green light emission is hardly observed for a homostructure of GaP layer thinner than 10μm at 77K. Even for the structures with relatively thick luminescent GaP layer, from GaP-$Al_xGa_{1-x}P$ double heterostructures, the efficiencies of green light emission via free exciton recombination are at least 10 times and 2 times higher than those from GaP homostructures at 77K and at room temperature, respectively.

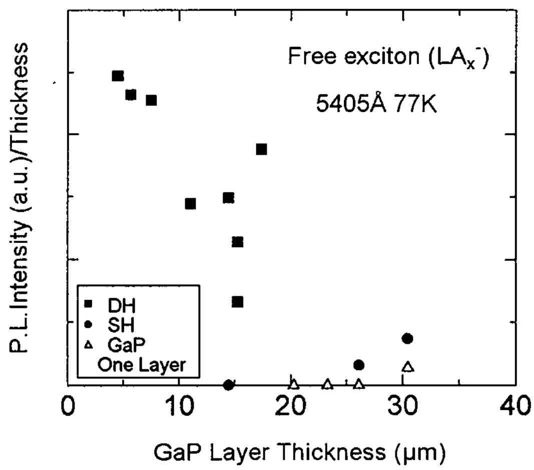

Fig.3 P.L. Intensity Dependence on GaP Layer Thickness

2. The barrier confinement effect of free excitons in double heterostructures of GaP and $Al_xGa_{1-x}P$ is effective when the luminescent layer GaP is thinner than the diffusion length of excess free carriers. The diffusion length of free excitons is about 20μm at 77K and 13μm at room temperature, the lifetime of free exciton is about 0.6μs at 77K and 0.25μs at room temperature as a result of rough evaluation.

3. Room temperature luminescence in $Al_xGa_{1-x}P$-GaP heterostructures is dominantly from phonon assistant free exciton recombinations as the result of discussion on photoluminescence spectra at different temperatures.

4. Free exciton recombination luminescence intensity of $Al_xGa_{1-x}P$-GaP heterostructures increases with temperature, greatly different from the ones of bound exciton and donor-acceptor.

5. Free exciton recombination luminescence intensities show an enhancement tendency when doped with the shallow donor impurity tellurium up to $2.5 \times 10^{17}cm^{-3}$ in the GaP layers of heterostructures. The shallow donors are thought to aid the free exciton formation and recombination by providing free electrons. There is also a possibility that free exciton recombination probability is increased by the presence of shallow impurity atoms.

6. A result that deep level concentration is directly proportional to root of donor impurity density ($N_t \propto N_D^{\frac{1}{2}}$), reveals the close connection of deep level concentration to shallow donor impurity density, showing that nonradiative centers are produced when tellurium is doped in GaP.

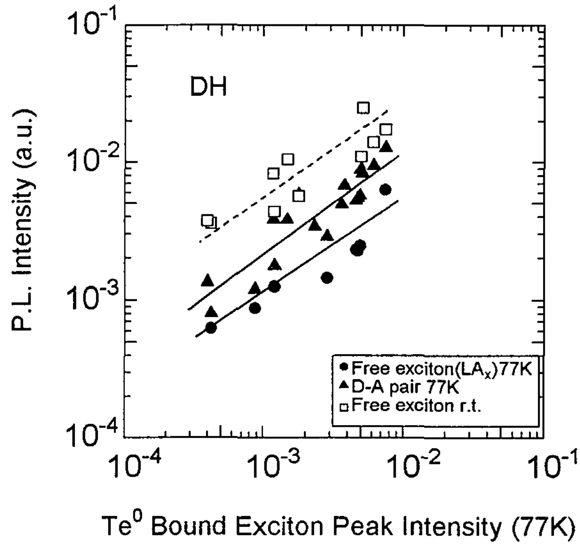

Fig.4 P.L. Intensity Dependence on Te^0 Peak Intenaity

Chapter 5 is the conclusion of this thesis research. As a basic research of light emitting diode, this thesis provides useful results in following two aspects:

With TDM-CVP LPE, $Al_xGa_{1-x}P$ alloy semiconductor as a shorter wavelength green light emitting material is applicable. Its green light emitting mechanism of free exciton recombination with and without phonon assistance known from this research, will be the basis in developing $Al_xGa_{1-x}P$ LEDs.

GaP light emitting efficiency is increased in $Al_xGa_{1-x}P$-GaP heterostructures, and more obviously in double heterostructures. It can be predicted that with proper shallow impurity doping, a high brightness of green band luminescence can be realized in optimized $Al_xGa_{1-x}P$-GaP double heterostructures.

審査結果の要旨

蒸気圧制御温度差法（TDM-CVP）液相成長法によるGaP 純緑色発光ダイオードは量産化技術が確立しており、低廉であることが特徴であるが、GaP が間接遷移型半導体であるため、直接遷移型半導体に比べて発光効率が十分でない。そこで、発光効率の更なる向上が求められている。また、発光波長もフルカラー表示用には、現在の 555nm より、更に短波長化することが求められている。著者は、GaP との格子整合性が良い $Al_xGa_{1-x}P$ を活用し、その緑色発光機構を明らかにすることにより短波長化と発光効率向上の指針を得た。本研究はその成果をまとめたもので全文５章よりなる。

第１章は序論であり、本研究の背景と目的を述べている。

第２章では、TDM-CVP 液相成長法による $Al_xGa_{1-x}P$ エピタキシャル層の成長法、および、$Al_xGa_{1-x}P$-GaP 単一ヘテロ（SH）エピタキシャル層、二重ヘテロ（DH）エピタキシャル層の成長法について記述している。また、フォトルミネセンス（PL）および吸収スペクトルの測定法について記述している。

第３章では、種々の Al 組成で $Al_xGa_{1-x}P$ 単一層を成長し、組成均一性が良好であることを確認した。各組成においてフォトルミネセンスを測定した結果、Al を添加しない場合には観測されない新たなスペクトル線が現れ、これが無フォノン自由励起子再結合によることを初めて明らかにした。また、低温から室温までフォトルミネセンススペクトルを測定し、無フォノン自由励起子再結合が室温での主要な発光機構となること、少なくとも 550nm から 540nm まで短波長化が可能であることを示した。

第４章では、GaP LED の発光効率を高める方法として $Al_xGa_{1-x}P$-GaP 単一ヘテロ（SH）構造および、二重ヘテロ（DH）構造の採用を提案し、SH,DH エピタキシャル層を成長し、フォトルミネセンス測定を行った結果を述べている。従来の構造である GaP 単一層の場合は、膜厚 20μm 以下になると全く発光が見られないのに対し、DH 構造では膜厚 4 μm 以下において最も強く自由励起子発光を生じることを見いだし、自由励起子及び正孔が電位障壁内に閉じこめられる効果が発揮されていることを確認した。更に、SH,DH エピタキシャル層に、浅い不純物である Te を種々のレベルで添加し、$1x10^{17}cm^{-3}$ までは添加量に比例して室温自由励起子発光強度が増大することを明らかにした。

第５章は結論である。

以上要するに本論文は、GaP との格子整合性が良い $Al_xGa_{1-x}P$ を活用した $Al_xGa_{1-x}P$-GaP 系の緑色発光機構を明らかにすることにより短波長化と発光効率向上の指針を得たもので、電子材料学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。